

PHOTO-ADDRESSABLE SUBSTRATES AND PHOTO-ADDRESSABLE SIDE-GROUP
POLYMERS WITH HIGHLY INDUCIBLE DOUBLE REFRACTION
[Schnell fotoadressierbare Substrate sowie fotoadressierbare
Seitengruppenpolymere mit hoher induzierbarer Doppelbrechung]

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UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. July 2009

Translated by: FLS, Inc.

PUBLICATION COUNTRY	(19):	WO
DOCUMENT NUMBER	(11):	97/44365
DOCUMENT KIND	(12):	A1
PUBLICATION DATE	(43):	19971127
APPLICATION NUMBER	(21):	PCT/EP97/02489
APPLICATION DATE	(22):	19970515
ADDITION TO	(61):	
INTERNATIONAL CLASSIFICATION	(51):	C08F 8/00
PRIORITY	(30):	May 22, 1996[DE] 19620588.3
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TITLE	(54):	PHOTO-ADDRESSABLE SUBSTRATES AND PHOTO-ADDRESSABLE SIDE-GROUP POLYMERS WITH HIGHLY INDUCIBLE DOUBLE REFRACTION
FOREIGN TITLE	[54A]:	Schnell fotoadressierbare Substrate sowie fotoadressierbare Seitengruppenpolymere mit hoher induzierbarer Doppelbrechung

Rapidly photo-addressable substrates and photo-addressable side-group polymers with highly inducible double refraction

This invention relates to a method for extremely rapid writing on photo-addressable substrates, substrates prepared for this method, and the use of such substrates in information technology. This invention also relates to photo-addressable side-group polymers, in which high double refraction can be induced by irradiation, making them suitable for storing optically available information or for producing passive or optically switchable components.

Photo-addressable polymer are known (Polymers as Electrooptical and Photooptical Active Media, V. P. Shibaev (ed.), Springer Verlag, New York, 1995). Particularly suitable for this purpose are side-group polymers, the group of copolymers being distinguished by a very broad possible range of variation in properties. Their main salient feature is that their optical properties, such as absorption, emission, reflection, double refraction, and scattering, can be reversibly changed by light-induced means. Such polymers have a special branched structure: Their linear backbone contains side groups, joined by molecular parts that act as spacers, that can absorb electromagnetic radiation. Examples of this type are the side-group polymers containing azobenzene groups, in accordance with US-PS 5,173,381. These substances are characterized by the ability to form directed double refraction when irradiated with polarized light. The double refraction patterns that are written in can be made visible in polarized light.

It is also known that man a locally limited double refraction, whose preferred axis moves with the rotation of the polarization direction, can be inscribed with polarized light in layers of these polymers at an arbitrary position (K. Anderle, R. Birenheide, M. Eich, J. H. Wendorff, Makromol. Chem., Rapid Commun. 10, 477 - 483 (1989), J. Stumpe et al., 20. Freiburger Arbeitstagung Flüssigkristalle 1991). These processes are slow. Of course, in some cases after just a few seconds of exposure time the beginning of anisotropic behavior can be determined, but minutes to hours are generally needed for the effect to reach the maximum that may be achieved. Here, the time that is used is approximately proportional to the magnitude of the effect. One feature of optical addressing is that the optical axis of the inscribed double refraction is perpendicular to that of the inscribing polarized light. The simple possibility of optically erasing inscribed information by rotating

* Number in the margin indicates pagination in the foreign text.

the polarization direction of the inscribing light is based on this property. In this case, writing and erasing are equally rapid; apart from the direction of polarization of the light that is used, they are identical processes. In contrast to this is the process of thermal erasing by heating the layer over the glass transition temperature of the polymer, at which all information is erased at once.

Information representation, storage, and processing follow two basically different paths, which are called serial and analog. In the analog method, all information is acquired and converted at the same time. A typical example of this is photography, which uses the silver halide film as an analog recording medium. This case applies to the exposure of a layer of photo-addressable polymers with polarized light through a master pattern. Since all points of the image are developed at the same time, the inscription (development) time is seldom critical in these processes. With serial processes, on the other hand, the pieces of information are called up one after the other. For objects with a very high information density, such as images, very high number of these image points must at times be inscribed one after the other, so that the development time is the sum of the development times of the individual image points. Consequently, it is extremely important in this case to have a high inscription rate, while maintaining sufficient stability of both the initial state of the unscribed regions and the final state of the inscribed regions. In both processes, the exact reproduction of gradations in the differences in brightness (gray scale values) of the pattern is extremely important. To date, it has not been possible to solve the problem of high inscription rates via the optical path in a technically satisfactory manner, since there are significant boundary conditions present in addition to the information transfer rate. Most important of these are stability, erasability, and the gray-scale capability. There are fundamental reasons for this.

As a general rule, only systems in which no mass is changed, but only fields or vectors, can react very rapidly to control commands. When mass is moved, i.e. in rearrangement processes or chemical reactions, the reaction is orders of magnitude slower and is determined in part by the viscosity of the medium. Thus, the maximum switching time of the low-viscosity twisted nematic cells is in the msec range, while a side group copolymer requires minutes, often many hours, to reach its maximum obtainable double refraction.

If we do not require reversibility of the inscribed changes, then any desired energy density may be chosen, locally destroying the substrate in the extreme case. Such materials are described, for example, by G. Kämpf in Kirk-Othmer, Encyclopaedia of Chemical

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Technology, 4th ed., 14, 277-338 (1995). However, there are several disadvantages to this method, which has been described in the literature in numerous variations. The most important of these is that the process entails a significant intrusion into the structure of the substrate and the hole that is formed is basically unstable. Moreover, there is always the problem of evaporated material, which is deposited somewhere in the apparatus or on the storage medium and, finally, very high laser energy densities are required, generally $> 10^7$ mJ/m².

Since preservation of the substrate is also a condition for reinscription on it, the light intensity cannot be increased indefinitely; moreover, the decomposition conditions must not be exceeded. Thus, there is an upper energy-density limit that is defined by the stability of the material. The smallest amount of energy needed to produce a detectable and stable change in the layer has been determined by Coles (using polysiloxane) at 4×10^5 mJ/m² (C. B. McArdle in Side Chain Liquid Crystal Polymers, ed: C. B. McArdle, Blackie, Glasgow 1989, p. 374). Assuming that the minimum energy for polymer substrates lies in that same order of magnitude, then if the object is to handle the substrate gently, the side-group polymers must be inscribed slowly (since the minimum energy is close to the decomposition energy), so that real-time serial storage appears to be unsuitable. To date, this fundamental disadvantage has stood in the way of technical application and it is the object of the present invention to remedy this deficiency.

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Surprisingly, we have now found that extremely rapidly addressable storage media can be produced from photo-addressable polymers that are slow per se by irradiating the substrates over a large surface using a light source that is suitable for conventional inscription, so that optical anisotropy is produced. Optical anisotropy means that the propagation velocity of the light in the plane of the layer is direction dependent. This creates direction-dependent refractive indices, so-called double refraction. If the substrates prepared in this way are briefly irradiated with suitably intense light, the double refraction is varied extremely rapidly and permanently, i.e. it is reduced or entirely eliminated. The degree of residual double refraction can be adjusted, depending on the light intensity.

Thus, there are two optical processes that differ in their effect: In a first, generative process, the layer must first become anisotropically double refractive over its surface. The double refraction (optical anisotropy) is typically given as the difference, Δn , in the maximum, direction-dependent refractive indices, n , at a certain wavelength.

Any light source for polarized light is suitable for generating double refraction over a large surface, for example an incandescent lamp followed by a polarization foil or preferably a laser. Essentially, the time required depends only on the power density of the light source, with no lower limit being known at present. The upper limit for the power density of the light source is determined by the threshold of destruction of the material; this depends on the material and is in the range of 10^7 to 10^8 mW/m². The material can be addressed over a large surface in a structureless or selective manner, for example through a mask; structureless addressing is preferable, however, particularly if it extends over the entire substrate surface. The optical anisotropy, Δn , of the first process, which is necessary for the purposes of the invention, can be very small; the only requirement is that it be measurable. The anisotropy, Δn , produced in the first process preferably is at least 0.001, in particular at least 0.005; it is preferably a maximum of 0.95, in particular a maximum of 0.8. /5

The second optical process relates to the use of substrates prepared in the first optical process and comprises addressing the material that has been made anisotropically double refractive using light of very brief duration. The inscribing light now has a different quality: It can be polarized or nonpolarized. Polarized light whose axis is parallel to that of the substrate is preferred. The energy density should generally be 10^3 to 10^7 , preferably 10^5 to $6 \cdot 10^5$ mJ/m². "Brief" means that the effect of the light can last 10^{-15} to 10^{-3} , preferably 10^{-10} to 10^{-5} s. The light source must be fast enough so that laser light sources are preferable. With this method, sequential inscription speeds of up to 100 MHz, preferably 5 to 50 MHz, are possible. With sequential addressing, the absorption of photons in the material occurs quite rapidly, to be sure, but afterward enough time is available for a dark reaction.

Erasure can occur over a large surface, so that an unstructured pattern results. Preferred, however, are patterns with structures that have in the direction of their least extension a diameter of 10 nm to 20 μ m, in particular 10 nm to 1 μ m.

The inscribed information is stable, i.e., after the light source has been turned off, there is a storable, double refraction pattern that can be read with the help of polarized light. The change in brightness is proportional to the effect of the light. The material is gray-scale capable. The inscribed information is reversible, i.e., the information can be erased and a new inscription made.

Thus, the subject matter of the present invention is the use of surface structures made of photo-addressable polymers, having an optical anisotropy, Δn , of 0.001 to 0.95 for storing optically available information by partially selective variation of the optical anisotropy. Moreover, the subject matter of the present invention is a method for storing patterns in the surface structures to be used in accordance with this invention by exposure to light with an energy density of 10^3 to 10^7 mJ/m² for a time of 10^3 to 10^{15} s.

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For the purposes of this invention, the term "optical anisotropy" means a difference, Δn , in the maximum, direction-dependent refractive indices of at least 0.001 at a wavelength that is 30 nm shorter than the point at which the absorption in the longwave flank of the longest wave absorption peak is still 1% (absorption peak = 100%). The highest possible anisotropy values are desired, since they allow good results, even at very low layer thicknesses. Preferred values of Δn lie in the range of 0.05 to 0.95, in particular 0.1 to 0.8.

Further subject matter of the present invention are polymers in which optical anisotropy can be produced by pretreatment, which can be varied by exposure for a time of 10^3 to 10^{15} s.

Suitable polymers for producing the photo-addressable substrates are those in which a directed double refraction can be inscribed (Polymers as Electrooptical and Photooptical Active Media, V. P. Shibaev (ed.), Springer Verlag, New York 1995; Natansohn et al., Chem. Mater. 1993, 403-411). These include, in particular, side-group polymers, the copolymers of which are preferable. Preferred copolymers of this kind are described, for example, in DE-OS 43 10 368 and 44 34 966. The preferably contain a poly(meth)acrylate main chain serving as a backbone, with recurring units

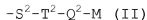
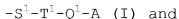


where R stands for hydrogen or methyl, the dots indicate the connection of additional units of the main chain and the side chain is connected to the carbonyl group.

Further subject matter are polymers with side chains of the structures described below.

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The side chains branching from the main chain can be of the formulas:



where

S^1, S^2 are, independently of one another, the atoms O, S, or the radical NR^1 ,

R^1 is hydrogen or C_1 - C_4 alkyl,

T^1, T^2 are, independently of one another, the radical $(CH_2)_n$, which may optionally be interrupted by $-O-$, $-NR^1-$ or $-OsR^1_2O-$ and/or substituted by methyl or ethyl,

n represents the number 2, 3, or 4,

Q^1, Q^2 is a divalent radical,

A is a unit capable of absorbing electromagnetic radiation, and

M is a polarizable aromatic group having at least 12 π -electrons.

Particularly preferable are polymers in which

Q^1, Q^2 are, independently of one another, Z^1, Z^2 or the group $-Z^1-X-Z^2-$, wherein Z^1, Z^2 are, independently of one another, the groups $-S-$, $-SO_2-$, $-O-$, $-COO-$, $-OCO-$, $-CONR^1-$, $-NR^1CO-$, $-NR^1-$, $-N=N-$, $-CH=CH-$, $N=CH-$, $-CH=N-$, or the group $-(CH_2)_m-$, where $m = 1$ or 2 , and

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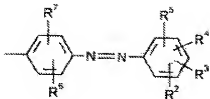
X is a 5 or 6 membered cycloaliphatic, aromatic, or heterocyclic ring and, for the case in which $Z^1 = -COO-$ or $-CONR^1-$, a direct bond or the group $-(CH=CH)_m-$,

where m has the meaning indicated above,

A is the radical of a monoazo dye that absorbs in the wavelength range of 650 to 340 nm, and

M is the radical of a polarized and further polarizable aromatic, linear system having at least 12 π -electrons.

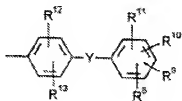
Preferred radicals A are those of the formula:



where

R^2 through R^7 are, independently of one another, hydrogen, hydroxyl, halogen, nitro, cyan, C_1-C_4 alkyl, C_1-C_4 alkoxy, CF_3 , CCl_3 , CBr_3 , SO_2CF_3 , C_1-C_6 alkylsulfonyl, phenylsulfonyl, C_1-C_6 alkylaminosulfonyl, phenylaminosulfonyl, aminocarbonyl, C_1-C_6 alkylaminocarbonyl, phenylaminocarbonyl, or $COOR^1$.

Preferred radicals M correspond to the formula



Where

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R^8 through R^{13} , independently of one another, are hydrogen, hydroxyl, halogen, nitro, cyan, C_1-C_4 alkyl, C_1-C_4 alkoxy, CF_3 , CCl_3 , CBr_3 , SO_2CF_3 , C_1-C_6 alkylsulfonyl, phenylsulfonyl, C_1-C_6 alkylaminosulfonyl, phenylaminosulfonyl, aminocarbonyl, C_1-C_6 alkylaminocarbonyl, phenylaminocarbonyl, or $COOR^1$ and

Y is $-COO-$, $-OCO-$, $-CONH-$, $-NHCO-$, $-O-$, $-NH-$, $-N(CH_3)-$ or a single bond.

Amorphous polymers are preferably, i.e., those that form no macroscopically perceptible liquid crystalline phases. "Amorphous" means an optically isotropic state. Such polymers neither scatter visible light nor possess double refraction.

The compounds can be prepared in a conventional manner by copolymerization of mesogen-containing and dye-containing monomers, by polymer-like reactions, or by polycondensation. Preferred is the radical copolymerization of monomers, i.e., of monomers with mesogenic groups, on the one hand, and dye-containing groups, on the other, in suitable solvents, for example aromatic hydrocarbons such as toluene or xylene, aromatic halogenated hydrocarbons such as

chlorobenzene, ethers such as tetrahydrofuran and dioxane, ketones such as acetone and cyclohexanone, and/or amides such as dimethylformamide, in the presence of the usual radical-donating polymerization initiators, such as azodiisobutyronitrile or benzoyl peroxide at elevated temperatures, for example at 30 to 130°C, preferably 40 to 70°C, if possible with the exclusion of water and air. Purification can be accomplished by precipitation or reprecipitation of the resulting side-chain copolymers from their solutions, for example with methanol.

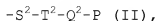
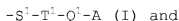
While groups that can absorb electromagnetic radiation generally absorb in the visible-wavelength region, the mesogenic groups of side-group polymers that are known to date possess a clearly shortwave absorption peak, preferably at wavelengths around 33,000 cm^{-1} ; the achievable double refraction changes are below 0.1. The methods thus far described for storing information by double refraction changes have generally been described as reversible, meaning that a temperature increased caused by light or heat can erase the stored information; the use of light can offer the advantage of locally limited erasability, so that this variant is often preferable. Of course, the basic erasability by adding energy in the form of heat contains, at the same time, the risk of a lack of thermal stability on the part of the inscribed information; in fact, this is a disadvantage of the known prior art. Thus, many compounds of this kind have the disadvantage that the inscribed double refractions are not temperature-stable; at elevated temperatures, in particular when temperatures approach the glass transition temperature, the double refraction becomes weaker and finally disappears completely. Thus, advantageous information carriers are those in which the stability of the inscribed information is as temperature-insensitive as possible. /10

It was found that superior side-chain polymers are produced when the side chains are selected in such a way that their absorption peaks are at a defined distance from one another. Information with high thermal stability can be inscribed in these new polymers using light.

Further subject matter of the present invention are therefore polymers having side chains of various types on a main chain, which serves as a backbone, both of which can absorb electromagnetic radiation (at least for one type: preferably having the wavelength of visible light), provided that the absorption peaks of the different side chains are at a distance of at least 200, preferably at least 500, and no more than 10,000, preferably no more than 9,000 cm^{-1} from one another.

Preferred polymers of this invention have on a main chain, which serves as a backbone, covalently bonded side groups of the formulas:

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where

S¹, S², independently of one another, are oxygen, sulfur, or NR¹,

R¹ is hydrogen or C₁-C₄ alkyl,

T¹, T², independently of one another, are the radical (CH₂)_n, which is optionally interrupted by -O-, -NR¹- or -OSiR₁₂O- and/or optionally substituted with methyl or ethyl,

n is the number 2, 3, or 4,

Q¹, Q², independently of one another, are a divalent radical,

A, P, independently of one another, are a unit capable of absorbing electromagnetic radiation,

provided that the absorption peaks of the radicals -Q¹-A and -Q²-P¹ are at least 200, preferably at least 500 and no more than 10,000, preferably no more than 9,000 cm⁻¹ from one another.

A significant characteristic of the invention is the recognition that the properties of the inventive polymers are better, the more similar the terminal groups -Q¹-A and Q²-P become to one another. This is true, in particular, with regard to their electronic configuration. The conformity of the orbital symmetry of the two groups should be great, but not 100%. By exciting the longer wavelength absorbing group in the first excited electron state (¹S₀), the orbital symmetries of the groups A and P become approximately antisymmetric.

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The function of the radicals T¹ and T² is to provide a certain spacing in the side-group ends from the chain serving as a backbone. For this reason, they are also called "spacers."

The radicals Q¹ and Q² join the end groups A and P to the spacers T¹ and T², which in turn make the connection to the main chain via the connecting element S¹ or S². The specific feature about the groups Q¹ and Q² is their influence on A and P, on the one hand, and on T¹ and

T^2 , on the other. The radicals Q^1 and Q^2 are therefore extremely important: thus, the similarity of the configuration, together with a relatively similar position of the absorption peaks of $-Q^1-A$ and $-Q^2-P$, can be achieved, for example, if identical radicals A and P are polarized to a different extent by different radicals Q^1 and Q^2 .

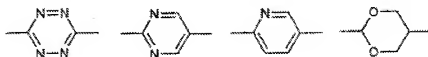
Preferred radicals Q^1 and Q^2 , independently of one another, contain the groups $-S-$, $-SO_2-$, $-O-$, $COO-$, $-OCO-$, $-CONR^1-$, $-NR^1CO-$, $-NR^1-$, $(CH_2)_m$, where $m = 1$ or 2 , a divalent 6-membered ring with optionally 1 to 2 N atoms (in this case the link to the radicals T^1 and A or T^2 and P occurs via these N atoms) and the group Z^1-X-Z^2 , where

Z^1 , Z^2 , independently of one another, are the groups $-S-$, $-SO_2-$, $-O-$, $-COO-$, $-OCO-$, $-CONR^1-$, $-NR^1CO-$, $-NR^1-$, $N=N$, $-CH=CH-$, $-N=CH-$, $-CH=N-$, or the group $-(CH_2)_m-$, where $m = 1$ or 2 , and

X is the naphthalene radical, a 5 or 6-membered cycloaliphatic, aromatic, or heterocyclic ring, the group $-(CH=CH)_m-$, where $m = 1$ or 2 , or a direct bond.

Particularly preferred radicals X include 2,6-naphthylene and 1,4-phenylene and heterocyclic radicals of the structures:

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If X stands for a 5-membered ring system, it may be carbocyclic or, preferably, heteroaromatic and contain up to 3 heteroatoms, preferably from the series of S, N, and O. Suitable representatives are, for example, thiophene, thiazole, oxazole, triazole, oxadiazole, and thiadiazole. Heterocycles with 2 heteroatoms are particularly preferable.

If X stands for the group $-(CH=CH)_m-$, then m preferably has the value 1.

If X stands for a direct bond, then oxalic acid derivatives or urea derivatives or carbamates are obtained (Z selected from Z^1 and Z^2).

The preferred meanings of Z^1-X-Z^2 are benzoic acid amide and benzoic acid ester radicals of the type $-O-C_6H_4-COO-$, $-O-C_6H_4-CO-NR^1-$,

$-\text{NR}^1-\text{C}_6\text{H}_4-\text{COO}-$, $-\text{NR}^1-\text{C}_6\text{H}_4-\text{CO}-\text{NR}^1-$, and fumaric acid ester and amide radicals of the type $-\text{OCO}-\text{CH}=\text{CH}-\text{OCO}-$ and $-\text{NR}^1-\text{CO}-\text{CH}=\text{CH}-\text{CO}-\text{NR}^1$.

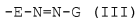
Q^1 stands more preferably for the groups $-\text{Z}^1-\text{C}_6\text{H}_4-\text{N}=\text{N}-$ und Q^2 for the group $-\text{Z}^1\text{C}_6\text{H}_4\text{CO}-\text{NH}-$.

The groups $-\text{Q}^1-\text{A}$ should possess absorption peaks in the wavelength range of 15,000 to 28,000 cm^{-1} and the groups $-\text{Q}^2-\text{P}$ should have absorption peaks in the wavelength range of 16,000 to 29,000 cm^{-1} . For the purposes of the present invention, A and P as well as Q^1 and Q^2 are defined in such a way that the longer-wave absorbing unit is called $-\text{Q}^1-\text{A}$ and the shorter-wave absorbing unit is $-\text{Q}^2-\text{P}$.

Preferred radicals A and P include radicals with one or more nuclei, such as cinnamic acid, biphenyl, stilbene, and azo dye radicals, benzoic acid anilides or analogs of the heterocyclic type, preferably monoazo dye radicals.

Particularly preferred radicals A and P correspond to the formula:

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where

G is a monovalent aromatic or heterocyclic radical and

E is a divalent aromatic or heterocyclic radical.

Aromatic radicals suitable as E preferably contain 6 to 14 C atoms in the aromatic ring, which may be singly or multiply substituted with C_1-C_{12} alkyl, C_1-C_{12} alkoxy, hydroxy, halogen (in particular F, Cl, Br), amino, nitro, trifluormethyl, cyan, carboxy, COOR (R= C_1-C_6 alkyl, cyclohexyl, benzyl, phenyl), C_5-C_{12} cycloalkyl, C_1-C_{12} alkylthio, C_1-C_6 alkylsulfonyl, C_6-C_{12} arylsulfonyl, aminosulfonyl, C_1-C_6 alkylaminosulfonyl, phenylaminosulfonyl, aminocarbonyl, C_1-C_6 alkylaminocarbonyl, phenylaminocarbonyl, C_1-C_4 alkylamino, Di- C_1-C_4 alkylamino, phenylamino, C_1-C_5 acylamino, C_1-C_4 alkylsulfonylamino, mono- or di- C_1-C_4 alkylaminocarbonylamino, C_1-C_4 alkoxy-carbonylamino or trifluormethylsulfonyl.

Heterocyclic radicals suitable as E preferably contain 5 to 14 ring atoms, 1 to 4 of which are heteroatoms of the series of nitrogen, oxygen, and sulfur, where the heterocyclic ring system can

be singly or multiply substituted with C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, hydroxy, halogen (in particular F, Cl, Br), amino, nitro, trifluormethyl, cyan, carboxy, COOR (R = C₁-C₆ alkyl, cyclohexyl, benzyl, phenyl), C₅-C₁₂ cycloalkyl, C₁-C₁₂ alkylthio, C₁-C₆ alkylsulfonyl, C₆-C₁₂ arylsulfonyl, aminosulfonyl, C₁-C₆ alkylaminosulfonyl, phenylaminosulfonyl, aminocarbonyl, C₁-C₆ alkylaminocarbonyl, phenylaminocarbonyl, C₁-C₄ alkylamino, di-C₁-C₄-alkylamino, phenylamino, C₁-C₅ acylamino, C₁-C₄ alkylsulfonylamino, mono- or di-C₁-C₄ alkylaminocarbonylamino, C₁-C₄ alkoxy carbonylamino or trifluormethylsulfonyl.

Aromatic radicals suitable for use as G preferably contain 6 to 14 C atoms in the aromatic ring, which can be singly or multiply substituted with C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, hydroxy, halogen (in particular F, Cl, Br), amino, nitro, trifluormethyl, cyan, carboxy, COOR (R = C₁-C₆ alkyl, cyclohexyl, benzyl, phenyl), C₅-C₁₂ cycloalkyl, C₁-C₁₂ alkylthio, C₁-C₆ alkylsulfonyl, C₆-C₁₂ arylsulfonyl, aminosulfonyl, C₁-C₆ alkylaminosulfonyl, phenylaminosulfonyl, aminocarbonyl, C₁-C₆ alkylaminocarbonyl, phenylaminocarbonyl, C₁-C₄ alkylamino, Di-C₁-C₄-alkylamino, phenylamino, C₁-C₅ acylamino, C₆-C₁₀ aryl-carbonylamino, pyridylcarbonylamino, C₁-C₄ alkylsulfonylamino, C₆-C₁₂ arylsulfonylamino, mono- or di-C₁-C₄ alkylaminocarbonylamino, C₁-C₄ alkoxy carbonylamino, or trifluormethylsulfonyl.

Heterocyclic radicals suitable for use as G preferably contain 5 to 14 ring atoms, 1 to 4 of which are heteroatoms from the series of nitrogen, oxygen, and sulfur, where the heterocyclic ring system can be singly or multiply substituted with C₁-C₁₂ alkyl, C₁-C₁₂ alkoxy, hydroxy, halogen (in particular F, Cl, Br), amino, nitro, trifluormethyl, cyan, carboxy, COOR (R = C₁-C₆ alkyl, cyclohexyl, benzyl, phenyl), C₅-C₁₂ cycloalkyl, C₁-C₁₂ alkylthio, C₁-C₆ alkylsulfonyl, C₆-C₁₂ arylsulfonyl, aminosulfonyl, C₁-C₆ alkylaminosulfonyl, phenylaminosulfonyl, aminocarbonyl, C₁-C₆ alkylaminocarbonyl, phenylaminocarbonyl, C₁-C₄ alkylamino, di-C₁-C₄ alkylamino, phenylamino, C₁-C₅ acylamino, C₁-C₄ alkylsulfonylamino, mono- or di-C₁-C₄ alkylaminocarbonylamino, C₁-C₄ alkoxy carbonylamino or trifluormethylsulfonyl.

If the radical E or G is multiply substituted, then the number of substituents is determined by the number of possible substitution positions, the possibility of incorporating the substituents, and the properties of the substituted system. The aryl and acyl radicals can

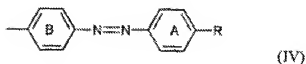
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optionally be substituted with nitro, cyano, halogen, C₁-C₄ alkoxy, or amino.

Particularly preferred -E-N=N-G radicals contain either an aromatic radical and a heterocyclic radical (i.e. either E or G are aromatic, the other radical heterocyclic) or two aromatic radicals (i.e., both E and G are aromatic).

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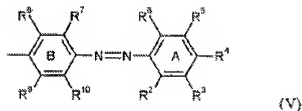
The preferred -E-N=N-G radicals are azobenzene radicals of the formula:



where

R stands for nitro, cyano benzamido, p-chloro-, p-cyano-, p-nitrobenzamido, or dimethylamino and the rings A and B can also be substituted.

Particularly preferred radicals A and P correspond to the formula:



where

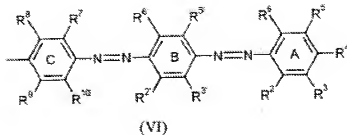
R² to R⁶, independently of one another, stand for hydrogen chlorine, bromine, trifluormethyl, methoxy, SO₂CH₃, SO₂CF₃, SO₂NH₂, or N(CH₃)₂, preferably nitro, cyano, or p-chloro-, p-cyano-, or p-nitrobenzamido, provided that at least one of these radicals is not hydrogen, and

R⁷ to R¹⁰, independently of one another, are hydrogen, chlorine, or methyl.

If the ring A is multiply substituted, then the 2,4- and 3,4-positions are preferable.

Other preferred radicals A and P correspond to the formula:

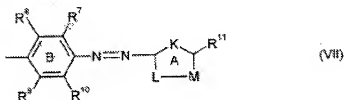
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where

R^2 through R^6 and R^7 through R^{10} have the meanings indicated above and $R^{2'}$ through $R^{6'}$ have the meanings of R^2 to R^6 , but are independent of the latter.

Other preferred radicals A and P correspond to the formula:



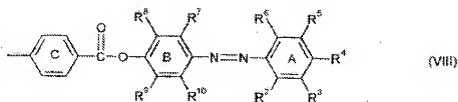
where

K, L, and M, independently of one another, are the atoms N, S, or O or optionally $-CH_2-$ or $-CH=$, provided that at least one of the members K, L, M is a heteroatom and the ring A is saturated or has 1 or 2 double bonds, and

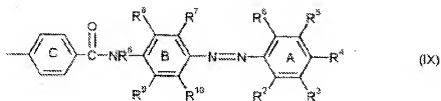
R^7 through R^{11} , independently of one another, have the meanings indicated above for R^7 to R^{10} .

The ring A preferably stands for a thiophene, thiazole, oxazole, triazole, oxadiazole, or thiadiazole radical.

Preferred radicals $-Q^1-A$ and $-Q^2-p$ correspond to the formulas: /18



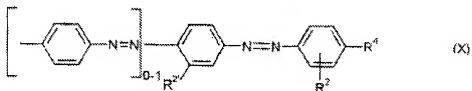
or



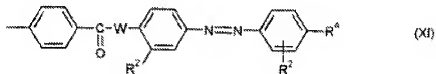
where

R^1 to R^{10} have the meanings indicated above.

Preferred groups A and P correspond to the formulas:



and



where

R^2 is hydrogen or cyano,

$R^{2'}$ is hydrogen or methyl,

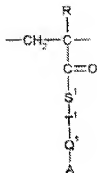
W is oxygen or NR^1 , and

R^4 is nitro, cyano, benzamido, p-chloro-, p-cyano-, p-nitrobenzamido or dimethylamino.

Common to the formulas above is the fact that substitutions in the 4-, 2,4-, and 3,4- positions of the ring A are particularly preferable.

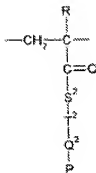
For these preferred groups A and P, preferred groups $-S^1-T^1-Q^1-$ and $-S^2-T^2-Q^2-$ correspond to the formulas $-OCH_2CH_2O-$, $-OCH_2CH_2OCH_2CH_2O-$, and $-OCH_2CH_2-NR^1-$.

The preferred polymers in accordance with this invention contain only repeating units with the side groups I and II, namely preferably those of the formulas:



(XII)

and

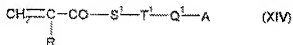


(XIII)

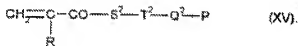
where R = H or, preferably, methyl.

Thus, the corresponding preferred monomers for introducing the side groups I and II correspond to the formulas:

/20



and



The side groups (I) and (II) are also preferably bound to (meth)acryloyl groups $CH_2=C(R)-CO-$, where R = hydrogen or methyl.

The main chain of the side-group polymers is preferably made of monomers that carry the side groups (I), monomers that carry the side group (II), and optionally additional monomers, where, in particular, the proportion of monomers that have the side group (I) is 10 to 95 mol%, preferably 20 to 70 mol%, the proportion of monomers that have the side group (II) is 5 to 90 mol%, preferably 30 to 80 mol%, and the proportion of additional monomers is 0 to 50 mol%, in each case with reference to the sum of all incorporated monomer units.

Possible "additional" repeating units are all components that can be chemically incorporated into the side-group polymer. Essentially, their only purpose is to reduce the concentration of the side groups I and II in the polymer, thereby creating a quasi "dilution" effect. In the case of poly(meth)acrylates, the "additional" monomers include ethylenically unsaturated copolymerizable monomers that preferably carry α -substituted vinyl groups or β -substituted allyl groups, preferably styrene, but also, for example, nucleus-chlorinated and alkylated or alkenylated styrenes, where the alkyl groups can contain 1 to 4 carbon atoms and the alkenyl groups 2 to 4 carbon atoms, such as vinyl toluene, divinyl benzene, α -methyl styrene, tert-butyl styrene, chlorostyrene, vinyl esters of carboxylic acids with 2 to 6 carbon atoms, preferably vinyl acetate; vinyl pyridine, vinyl naphthalene, vinyl cyclohexane, acrylic acid and methacrylic acid and/or their esters (preferably vinyl, allyl, and methallyl esters) with 1 to 4 carbon atoms in the alcohol components, their amides and nitriles, maleic acid anhydride, semi-esters, and diesters with 1 to 4 carbon atoms in the alcohol components, semi-amides and diamides and cyclic imides such as N-methyl maleinimide, or N-cyclohexyl maleinimide; allyl compounds such as allyl benzene and allyl esters, such as allyl acetate, phthalic acid diallyl esters, isophthalic acid diallyl esters, fumaric acid diallyl esters, allyl carbonates, diallyl carbonates, triallyl phosphate, and triallyl cyanurate.

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Preferred "additional" monomers correspond to the formula:



where

R^{12} stands for an optionally branched $\text{C}_1\text{-C}_6$ alkyl radical or a radical having at least one additional acrylic radical.

The inventive polymers can also contain more than one side group that corresponds to the definition of (I) or more than one side group that corresponds to the definition of (II) or several side groups of the definition of both (I) and (II).

The inventive polymers preferably have glass transition temperatures, T_g , of at least 40°C . The glass transition temperature can be determined, for example, in accordance with B. Vollmer,

Grundriss der Makromolekularen Chemie [Principles of Macromolecular Chemistry], pp. 406 - 410, Springer-Verlag, Heidelberg, 1962.

The inventive polymers generally have a molecular weight, determined as weight average, of 3,000 to 2,000,000, preferably 5,000 to 1,500,000, determined by gel-permeation chromatography (calibrated with polystyrene).

The structural elements with high shape anisotropy and high anisotropy of molecular polarizability are required for high optical anisotropy values. Using the structure of the polymers, the intermolecular interactions of the structural elements (I) and (II) are adjusted such that the formation of liquid-crystalline ordered states is suppressed and optically isotropic, transparent non-scattering films can be produced. On the other hand, the intermolecular interactions are still strong enough so that, when irradiated with polarized light, a photochemically induced, cooperative, directed reorientation process of the side groups is produced.

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Extremely high values of optical anisotropy can be induced in the optically isotropic, amorphous polymers of this invention by exposing them to polarized light. The measured values of the change in double refraction, Δn , lie between 0.05 and 0.8.

Linear polarized light with a wavelength in the region of the absorption bands of the side groups is preferably used as the light source.

Additional subject matter of the present invention are polymers in which polarized light can be used to inscribe double refraction changes, Δn , of over 0.15, preferably over 0.2, in particular over 0.4. The value, Δn , should be determined as described below:

First, the respective absorption peak $\lambda_{\max 1}$ or $\lambda_{\max 2}$ is determined for the two homopolymers. A change in double refraction is produced by exposing a film of the copolymer being tested using linear polarized light having a wavelength of $(\lambda_{\max 1} + \lambda_{\max 2}):2$. For this purpose, the samples are irradiated with polarized light in the direction normal to the surface. The power of the light source should be 1,000 mW/cm²; if the copolymer is destroyed under these conditions, then the light-source power is reduced in 100 mW steps until the copolymer is no longer destroyed by the exposure. The irradiation is continued until the double refraction no longer changes. The double refraction change is measured with a readout wavelength of $[(\lambda_{\max 1} + \lambda_{\max 2}):2] + 350 \pm 50$ [nm]. The polarization of the measuring

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light should form an angle of 45° relative to the polarization direction of the inscribing light.

The side-group monomers can be prepared and polymerized using methods known from the literature; cf., for example, Makromolekulare Chemie 187, 1327-1334 (1984), SU 887 574, Europ. Polym. 18, 561 (1982), and Liq. Cryst. 2, 195 (1987), DD 276 297, DE-OS 2831 909 and 3808430. The polymers in accordance with this invention are generally prepared by radical copolymerization of the monomers in suitable solvents, e.g. aromatic hydrocarbons such as toluene or xylene, aromatic halogenated hydrocarbons such as chlorobenzene, ethers such as tetrahydrofuran or dioxane, ketones such as acetone or cyclohexanone, and/or dimethyl formamide in the presence of radical-donating polymerization initiators, such as azobis(isobutyronitrile) or benzoyl peroxide, at elevated temperatures, typically 30 to 130°C , preferably 40 to 70°C , if possible at the exclusion of water and air. Isolation can occur by precipitation using suitable agents, such as methanol. The products can be purified by reprecipitation, using chloroform/methanol, for example.

Additional subject matter of the present invention is therefore a method for preparing the side-group polymers by copolymerization of the corresponding monomers.

The polymers are processed into layers with a thickness of 0.1 to 500 μm , preferably 1 to 30 μm , more preferably 2 to 10 μm . They may be cast from solution or applied by knife coating, dipping, or spin coating. They can form self-supporting films. Preferably, however, they are applied to backing materials. This can be accomplished by various known techniques, the method being selected based on whether a thick or thin layer is desired. Thin layers can be produced, for example, by spin coating or knife application from solutions or melt, while thicker ones are produced by melt pressing or extrusion.

Isotropic films are produced successfully without elaborate orientation methods using external fields and/or surface effects. They can be produced on substrates by spincoating, immersion, casting, or other easy coating methods, inserted between two transparent plates by pressing or flowing in, or simply produced as self-supporting films by casting or extrusion. Such films can also be produced by sudden cooling, i.e. by a cooling rate $> 100 \text{ K/min}$, or by rapid removal of the solvent, from liquid-crystalline polymers that contain structural elements in the sense described above.

Additional subject matter of the present invention are therefore films (both self-supporting and those made in the form of coatings)

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of the polymers described above and substrates coated with said films.

In the glass-like state of the polymers, the side-group polymers of this invention are optically isotropic, amorphous, transparent, and not light-scattering, and they can form self-supporting films.

Preferably, however, they are applied to substrate materials, such as glass or plastic films. This can be accomplished by various techniques that are known per se, the method being selected based on whether a thick or thin layer is desired. Thin layers can be produced, for example, by spin coating or knife application from solutions or melt, while thicker ones are produced by filling prefabricated cells, melt pressing, or extrusion.

The polymers can be used for digital or analog data storage in the broadest sense, for example for optical signal processing, for Fourier transforms and convolution, or in coherent optical correlation techniques. The lateral resolution is limited by the wavelength of the light used for inscription. It permits a pixel size of 0.45 to 3,000 μm , preferably a pixel size of 0.5 to 30 μm .

This property makes the polymers particularly suitable for processing images and for information processing by means of holograms, which are reproduced by illumination with a reference beam. Similarly, the interference pattern of two monochromatic coherent light sources can be stored with a constant phase relation. Accordingly, three-dimensional holographic images can be stored. Reading is accomplished by illuminating the hologram with coherent, monochromatic light. Due to the relationship between the electrical vector of the light and the associated preferred direction in the storage medium, a storage density can be achieved that is higher than in a purely binary system. With analog storage, gray-scale values can be adjusted continuously and with local resolution. Analog stored information is read in polarized light, whereby the positive or negative image can be retrieved, depending on the position of the polarizers. Here, on the one hand, the contrast of the film produced by the phase shift of the ordinary and extraordinary beams between two polarizers can be used, where the planes of the polarizers advantageously form an angle of 45° to the polarization plane of the inscribing light and the polarization plane of the analyzer is either perpendicular or parallel to that of the polarizer. Another possibility is detection of the deflection angle of the reading light produced by induced double refraction.

The polymers can be used as optical components that may be passive or actively switchable, particularly for holographic optics.

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Thus, the high light-induced optical anisotropy can be used for electrical modulation of the intensity and/or polarization state of light. Accordingly, components having imaging properties comparable to lenses or gratings can be made of a polymer film by holographic structuring.

The layers can be used for serial recording of photoconductive data of any kind, particularly images in the medical field.

Further subject matter of the present invention is therefore the use of the optically anisotropic substrates in information technology, in particular as components for storing and processing information, preferably images, and as holographic recording material.

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Unless otherwise indicated, the percentages indicated in the following examples relate in each case to the weight.

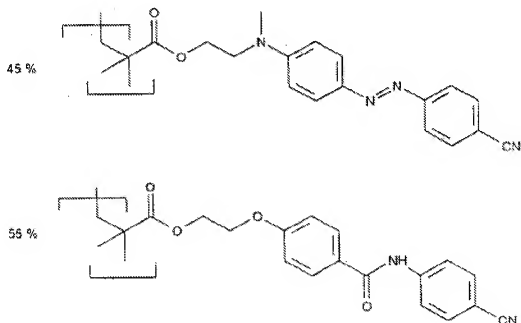
Examples

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Example 1

1.1 Pre-exposure

Glass plates measuring 2x2 cm were spin coated with a solution of the polymer units of the following formulas:



In order to achieve pre-exposure that is as homogeneous as possible, the plates were pre-exposed (distance: 2 cm) on a commercially available light box (Planilux, type LJ-S, light source: 2 fluorescent lamps (power: 15 watts each) connected to a film polarizer), after which the transmission values were determined between crossed polarizers. After 1 hour of pre-exposure 7.6% transmission was obtained and 13.7% transmission after 2 hours.

1.2. Inscribing and measuring setup

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For measuring the inscribed double refraction, a setup can be used consisting of a linearly polarized He-Ne laser, with downstream expansion optics, sample holder, rotatable polarization filter, and Ulbricht sphere with a photocell-power meter connected. The inscribed samples are aligned relative to the polarization direction of the He Ne laser in such a way that the angle to the polarization direction of the inscribing laser is 45°. The transmission direction of the polarization filter is perpendicular to the direction of the sampling He-Ne laser. In this configuration, the transmitted laser power is determined as a function of the inscribing power on the corresponding sample field. An additional measurement of the transmitted power on an unscribed sample site in the "open" position of the polarization filter is used for normalization.

1.3 Inscription

Flat surfaces (flat fields) are inscribed with the recorder arrangement mentioned above. The polarization direction of the inscribing laser was perpendicular to the transmission direction of the film polarizer used for pre-exposure. The data for the inscribing arrangement are:

Laser source: Ar-ion laser linearly polarized,

Single line operation, $\lambda = 514.5 \text{ nm}$

Laser power in the image plane, max 280 mW

Laser spot size 7-8 μm

Pixel size (line spacing) 5.4 μm

Scan length 7.41 mm

Scan height 5.82 mm

Scan rate (in direction of line) 0.6 to 23.8 m/sec

The exposure energy in the plane of the image is determined by both the laser power in the image plane and the scan rate.

The following change in transmission as a function of energy of the inscribing light is obtained (scan rate 23.8 m/sec; T = sample transmission in %, E = inscribing energy in [10^6 mJ/m²]) (see Figure 1). /29

The following characteristics can be derived from the measured data:

Total change in density in the inscribing range, $\delta = 0,9$

Gradation in the "linear" portion of the curve $g = 1.9$

Energy density for obtaining δD $E = 1.3 \times 10^6$ mJ/m²

The inscribed information is stable when stored at room temperature.

Examples 2-20

If, instead of the polymer used in example 1, a polymer having the repeating units indicated below is used and, otherwise, the method used in Example 1 is followed, then we find the following:

The symbols below have the following meanings in Tables 1, 2, 3, and 4:

R the substituents corresponding to formula 2, 3, 4, or 5,

λ the wavelength of maximum absorption,

Δn the change in double refraction in a first process,

x the content of antenna component in the copolymer,

E the inscribing energy, and

ε the optical density at the inscribing wavelength of 514 nm.

Repeating units:

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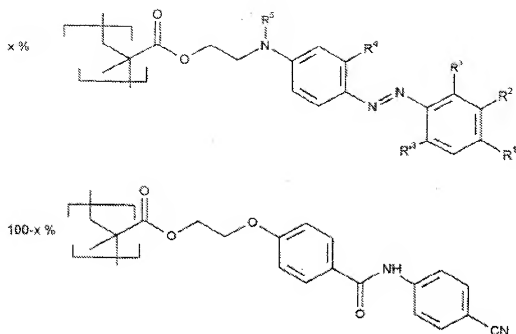


Table 1

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	R ¹	R ²	R ³	R ⁴	R ⁵	λ	Δn	α	T _g	E	κ	
2	CN	CN	H	H	CH ₃	Et	490	0.043	56	142	1.3	3.36
3	CN	H	H	H	H	Me	472	0.029	45	141	1.6	3.19
4	CN	H	CN	H	H	Me	490	0.077	59	144	1.8	2.5
5	NO ₂	H	CN	H	H	Me	490	0.057	49	129	1.9	1.8
6	NO ₂	H	H	H	H	Et	484	0.060	48.5	124	2	1.76
7	NO ₂	H	H	H	H	Me	469	0.116	44	136	2.1	3
8	NO ₂	H	H	H	H	Et	502	0.022	50	131	2.3	1.4
9	CH ₃	H	CN	CN	H	Me	403	0.039	51	120	2.4	3.38
10	CN	H	H	H	H	Me	436	0.074	58	138	2.7	2.13
11	CN	H	H	H	CH ₃	Et	408	0.03	50	114	2.8	3.43
12	CH ₃	H	H	H	H	Me	403	0.048	75	118	3.6	0.24
13	Cl	H	H	H	H	Me	412	0.042	60	99	3.7	0.51
14	CN	H	H	H	H	Me	452	0.019	75	133	4.1	1.75
15	Br	H	H	H	H	Me	416	0.016	52	137	4.2	1.51
16	CH ₃	H	H	H	H	Me	408	0.05	40	133	4.3	0.57
17	OCH ₃	H	CN	H	H	Me	414	0.032	56	133	4.3	0.3
18	OCH ₃	H	H	H	H	Me	407	0.039	45	128	4.5	0.2
19	OCH ₃	H	H	H	H	Me	406	0.041	60	123	4.5	0.24
20	OCH ₃	H	H	H	H	Me	410	0.028	28	132	5.7	0.19

Examples 21 - 30

If, instead of the polymer used in Example 1, a polymer having the repeating units indicated below is used and, otherwise, the method used in Example 1 is followed, then we find the following:

Meaning of the values in the tables, see Example 2:

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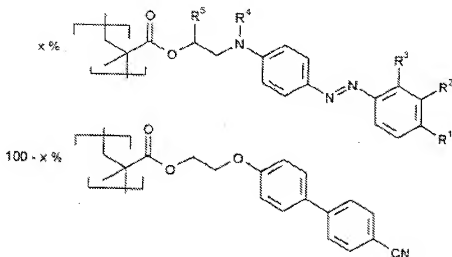


Table 2

	R ¹	R ²	R ³	R ⁴	R ⁵	λ	ΔE	α	E	ϵ
21	CN	H	H	Me	H	439	0.027	60	1.2	-
22	CN	H	CN	Me	H	502	0.038	40	1.4	3.34
23	CN	CN	H	Me	H	482	0.032	40	2.3	2.24
24	CN	H	H	Et	Me	446	0.023	40	2.3	1.7
25	CF ₃	H	H	Me	H	420	0.041	40	2.4	0.6
26	SO ₂ CF ₃	H	H	Me	H	460	0.096	40	2.5	1.91
27	OCH ₃	H	H	Me	H	407	0.034	40	1.4	0.2
28	CN	H	H	Me	H	450	0.029	40	4.5	-
29	CN	H	H	Me	H	450	0.024	40	4.8	-
30	OCH ₃	H	H	Me	H	412	0.014	60	6.6	0.18

Examples 31 and 32

If, instead of the polymer used in Example 1, a homopolymer having the repeating units indicated below is used and, otherwise, the method used in Example 1 is followed, then we find the following:

Meaning of the values in the tables, see Example2:

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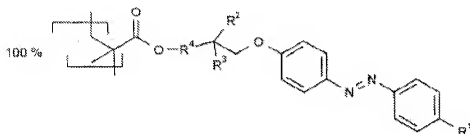


Table 3

	R ¹	R ²	R ³	R ⁴	λ	η	κ	E	n
31	CN	Me	H	-	365	0.055	100	3.5	0.2
32	CN	Me	Me	CH ₂	365	0.042	100	3.8	0.2

Examples 33 - 36

If, instead of the polymer used in Example 1, a polymer having the repeating units indicated below is used and, otherwise, the method used in Example 1 is followed, then we find the following:

Meaning of the values in the tables, see Example2:

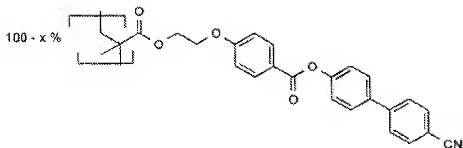
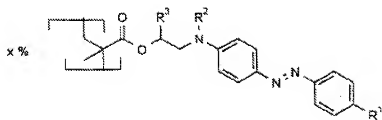


Table 4

	R ¹	R ²	R ³	λ	Δn	N	E	ϵ
33	CN	Et	Me	443	0.042	60	1.6	1.1
34	CN	Et	Me	444	0.039	50	1.8	1.1
35	CN	Et	Me	446	0.067	40	2.2	0.79
36	CF ₃	Me	H	420	0.032	60	2.2	0.4
37	CF ₃	Me	H	420	0.022	70	3.3	0.4

Example 38

A sample prepared as described in Example 1 is subjected to the following test cycle:

- 38.1 Pre-exposure of the sample on the light box with downstream polarization film (exposure time 1 hour)
- 38.2 Inscription with the recorder arrangement at various laser powers, with polarization of the writing laser perpendicular to the polarization of the pre-exposure
- 38.3 Renewed exposure of the inscribed sample on the light box with downstream polarization film, where the transmission direction of the polarizer is the same as in the first pre-exposure (exposure time. 7-8 hours)
- 38.4 Inscription with the recorder arrangement under the same conditions as those described above.

Transmission of the sample after renewed pre-exposure (see Figure 2)

Figure 2: sample transmission T in [%] after renewed pre-exposure, as a function of E [10^6 mJ/m²]:

Transmission at places where no thermal structures were inscribed: solid squares

Transmission at places where thermal structures were produced in the inscribing process: open squares

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Figure 3: Transmission of the sample after renewed inscription in [%], as a function of E [106 mJ/m²]

immediately after inscription: open squares

Initial situation after the "erasing exposure": solid squares (see Figure 3)

Conclusion:

The inscribed patterns can be completely erased by renewed pre-exposure at places where no thermal structures have been produced. However, thermally inscribed structures remain intact after erasing, reducing the sample transmission at the corresponding places by scattering.

With renewed inscription, the behavior of the sample is equivalent to the original inscription test, as demonstrated by the following Figure 4 (see Figure 4).

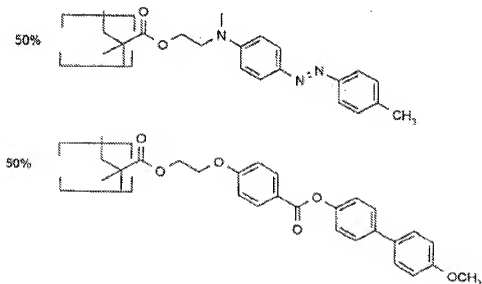
Figure 4: Normalized sample transmission, T [%], as a function of the inscribing energy, E_{in} [10^6 mJ/m²]

After the first inscription: filled squares

After the second inscription: open squares

Example 39

Two samples, prepared as in example 1 but using a polymer with repeating units of the formulas



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are pre-exposed as described in Example 1, namely one sample to a transmission of 49% and the other to 61%. The process as described in Example 1 is then followed, producing the decrease in transmission in [%] with increasing inscribing energy, E_{in} in [106 mJ/m²], depicted in Figure 5 below (see Figure 5).

Measured values from the "49% transmission" inscription test: filled squares;

Measured values from the "61% transmission" inscription test: open squares.

Example 40 Preparation of the polymers

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1.1 Preparation of the monomers

1.1.1 from methacrylic chloride

100 g N-methyl-N-(2-hydroxyethyl)-aniline is dissolved in 100 ml chloroform. 182.6 g triethylamine and 137.2 g methacrylic chloride are slowly added dropwise with stirring at 40°C and stirring is continued overnight at 40°C. 500 ml chloroform is then added to the reaction solution and the material is extracted 5 times, each time with 200 ml water. The organic phase is dried over anhydrous magnesium sulfate, copper (I) chloride is added, and after the solvent has been distilled off, the material is distilled under a high vacuum. The methacrylic ester of hydroxyethyl-aniline is distilled over at 127-130°C/55 mbar, in the form of a water-clear liquid. The yield is 49.5 g.

1.1.2 from methacrylic acid

50 ml conc sulfuric acid is added dropwise at room temperature with stirring to a solution of 100 ml N-methyl-N-(2-hydroxyethyl)-aniline, 265 ml methacrylic acid, and 26.5 g hydroquinone in 398 ml chloroform. After standing overnight, the material is heated and the reaction water is removed azeotropically. After cooling, the pH is adjusted to 7 - 8 using concentrated aqueous soda solution and the product is extracted from the solution by shaking with ether. The treatment is continued as described above, producing a yield of 56 g.

1.1.3 Monomer having the end group -A

7.15 g 2,4-dicyanoanilin is diazotized with 24 g nitrosyl sulfuric acid at 0 to 5°C in a solution of 100 ml glacial acetic

acid, 20 ml phosphoric acid, and 7.5 ml sulfuric acid and stirred for 1 h. The reaction mixture is added to a solution of 15.3 g N-methyl-N-(2-methacryloyloxyethyl)aniline and 1.5 g urea in 60 ml glacial acetic acid, while the temperature is maintained at 10°C. After brief stirring, soda is added to the reaction mixture to adjust the pH to 3, the precipitate is extracted by suction, washed with water, and dried. 14.4 g of a red solid is obtained, which can be used without further purification.

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1.1.4 Monomer having the end group -P

27.6 g 4-amino-2',4'-dicyanoazobenzene in 500 ml dioxane is added to a solution of 33 g 4-(2-methacryloyloxy)-ethoxy-benzoic acid chloride in 100 ml dioxane, stirred for 2 h, and the product is precipitated by pouring the solution into 2 liters water. The precipitate is suction filtered, dried, and purified twice by recrystallization from dioxane. The yield is 30.4 g of orange-red crystals with a melting point of 215-217°C.

1.2 Preparation of the copolymer

2.7 g of monomer 1.1.3 and 5.19 g of monomer 1.1.4 are brought to polymerization in 75 ml DMF under argon as a protective gas with 0.39 g azobis(isobutyronitrile) as a polymerization initiator at 70°C. After 24 h the material is filtered, the DMF distilled off, the residue boiled with methanol to remove the unreacted monomers, and dried under a high vacuum at 120°C. 7.18 g of an amorphous copolymer having a glass transition temperature of 144°C, whose optical properties are indicated in example 42.5, is obtained.

A similar method is used to produce other copolymers.

Example 41 Variation in the distance between absorption peaks

Preparation of the test samples: 2 x 2 cm glass plates 1.1 mm thick are placed in a spin coater (Süss RC5 model) and coated with 0.2 ml solution of 150 g of the following polymers in 1 liter absolute tetrahydrofuran at 2,000 RPM for 10 s. The coating is 0.9 µm thick, transparent, and amorphous. The surface is uniformly dark in daylight between crossed polarizers. No signs of polarizing areas are observed.

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The measurement plates are exposed to an Ar-ion laser with a power of 250 mW/cm² at a wavelength of 514 nm, producing a double

refraction. The maximum achievable double refraction, Δn , in the polymer layer is determined in two steps:

First the maximum inducible optical path difference, $\Delta \lambda$, that produces brightening between crossed polarizers is determined by measurement with an Ehringhaus compensator. The quantitative determination is made by compensation of the brightening. This is accomplished by rotating a quartz crystal placed in the optical path, altering the optical path length and, thus, the optical path difference. The optical path difference is then determined at which the brightening is fully compensated. The measurement must be made with light at a wavelength that lies outside the absorption region, in order to prevent resonance effects. In general, a He-Ne laser with an emission wavelength of 633 nm is sufficient, while at long absorption wavelengths light with a diode laser of wavelength 820 nm is used for measuring. The readout wavelength that is used is indicated in the tables below, under the column heading " λ ."

In a second step, the layer thickness of the polymer is measured using a mechanically acting layer thickness measuring device (Alphastep 200; manufacturer: Tencor Instruments)

The change in double refraction, Δn , is determined from the quotient of the optical path differences, $\Delta \lambda$, and the layer thickness, d :

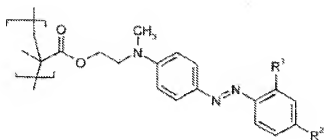
$$\Delta n = \frac{\Delta \lambda}{d}$$

The absorption peaks are determined by evaluating the UV/vis absorption spectra. In the case of extreme mixtures, only one peak may be evaluable. In these cases, the value that cannot be read must be replaced with the one of the corresponding 1:1 copolymer.

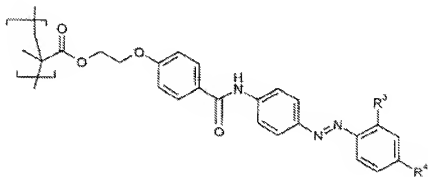
/40

A similar procedure is used for preparing the compounds and measuring the data in the following examples.

For the case in which $T^1=T^2$, $Q^1 \neq Q^2$, $A \neq P$:



m mol%



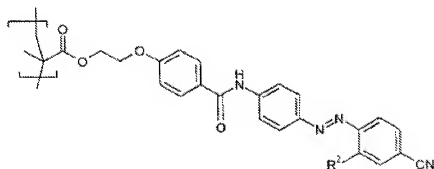
n mol%

Formula 2

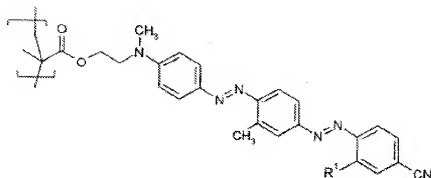
Beispiel	v_A	v_P	Δv_{P-A}	Δn	n	m	mW/cm^2	$\lambda[nm]$
$R^1=H; R^2=CN; R^3=CN; R^4=CN$								
41.1	22 900	25 300	2 600	0,110	70	30	250	820
$R^1=CN; R^2=CN; R^3=H; R^4=CN$								
41.2	20 300	27 100	6 800	0,183	60	40	60	633
41.3	20 400	26 700	6 300	0,136	40	60	60	633
$R^1=H; R^2=NO_2; R^3=H; R^4=CN$								
41.4	21 400	27 000	5 600	0,176	40	60	60	633
$R^1=NO_2; R^2=NO_2; R^3=CN; R^4=CN$								
41.5	19 300	25 600	6 300	0,190	70	30	250	820
$R^1=NO_2; R^2=NO_2; R^3=H; R^4=NO_2$								
41.6	18 000	26 700	8 700	0,106	70	30	250	820

Key: a) Example

m mol%



n mol%

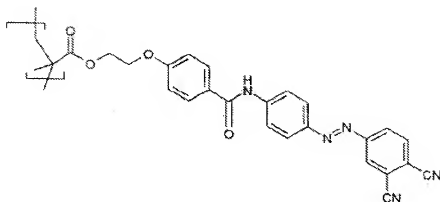


Formula 3

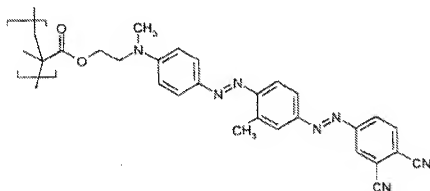
Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
a)								
$R^1=R^2=H$								
41.7	19 400	27 900	8 300	0,197	50	50	250	820
$R^1=H; R^2=CN$								
41.8	20 000	25 400	5 400	0,287	70	30	250	820
$R^1=CN; R^2=CN$								
41.9	19 000	25 900	6 900	0,295	60	40	250	820
$R^1=CN; R^2=H$								
41.10	19 000	27 400	8 200	0,318	40	60	250	820

Key: a) Example

m mol%



n mol%



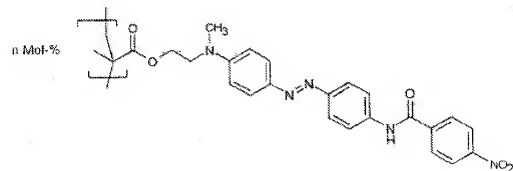
/43

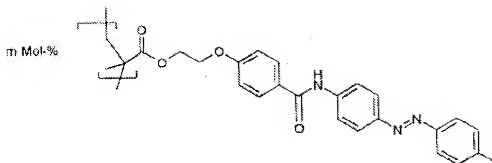
Formula 4

Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
4111	19200	27800	8600	0.148	50	50	250	820

Key: a) Example

Formula 5

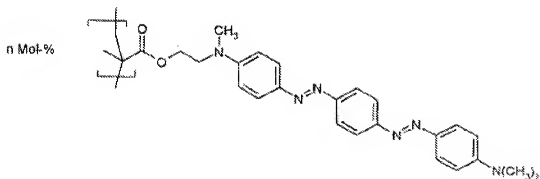
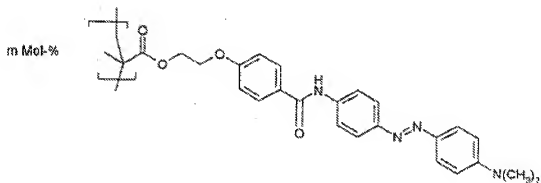




Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
41.12	20 700	26 000	5 300	0,120	50	50	250	820

Key: a) Example

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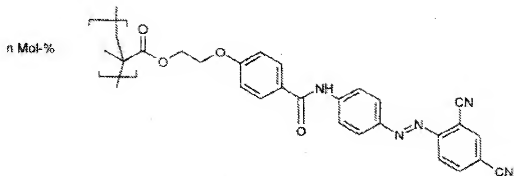


Formula 6

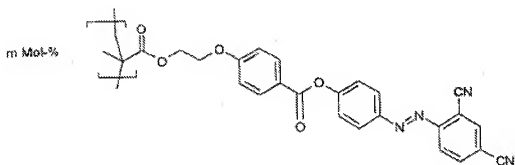
Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
a)	41.13	18 900	23 400	4 500	0,250	50	250	820

Key: a) Example

Example 42 $T^1 = T^2$; $Q^1 \neq Q^2$; A=P



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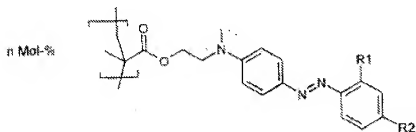


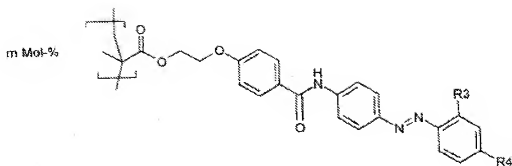
Formula 7

As in example 1, a copolymer of the formula 7 is prepared and a sample produced and measured as in Example 2. A double refraction change, Δn , is obtained, inscribed at 488 nm as follows:

Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
42.1	25 000	28 000	3 000	0,232	50	50	250	633

Key: a) Example]





Formula 8

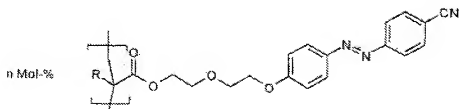
/46

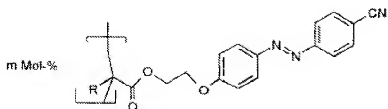
Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
$R^1 = R^2 = R^3 = R^4 = CN$								
42.2	20.400	25.800	5.400	0,175	90	10	120	633
42.3	20.400	25.400	5.000	0,231	80	20	60	633
42.4	20.400	25.300	4.900	0,414	70	30	60	633
42.5	20.400	25.000	4.600	0,158	60	40	120	633
$R^1 = R^3 = H, R^2 = R^4 = NO_2$								
42.6	19.200	26.700	7.500	0,171	70	30	250	820
42.7	19.800	25.600	5.800	0,145	50	50	250	820
42.8	21.300	25.000	2.700	0,116	30	30	250	820

Key: a) Example

Example 43 $T^1 \neq T^2$; $Q^1 = Q^2$, $A = P$

A copolymer of the following formula is produced, as in Example 1:





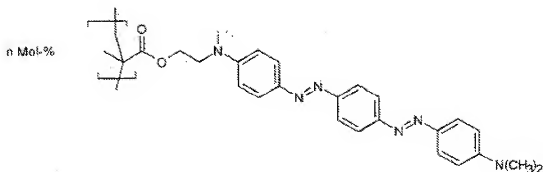
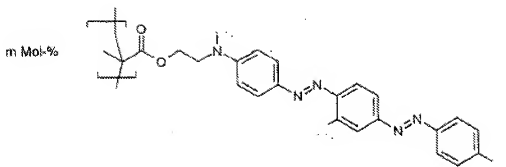
Formula 9.

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Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
R=CH ₃								
43.1	27 000	27 400	400	0,103	60	40	200	633
R=H								
43.2	27 600	28 300	500	0,104	60	40	200	633

Key: a) Example

Example 44 $T^1 = T^2$; $Q^1 = Q^2$, $A \neq P$



Beispiel	v_A	v_P	Δv_{P-A}	Δn	m	n	mW/cm ²	λ [nm]
44.1	21 600	23 400	1 800	0,211	50	50	60	633


Key: a) Example

Example 45 Heat resistance

Glass plates measuring 2 x 2 cm are coated as described in example 1 with a polymer in accordance with example 3.3 and 11 fields (flat fields) are inscribed in such a way that a series of increasing transmission between about 0 and 82% is produced, with approximately identical spacing. The transmission is determined immediately following inscription. This defines the initial state. This sample is allowed to stand in the dark for 2 months at room temperature, without additional protection. Then, in each case one additional plate is stored for 24 h at 60°C, 80°C, and 120°C in a drying cabinet and the transmission is determined once again. In this way, 4 series of values are obtained that are compared to the initial state. The following table 1 indicates these transmission values:

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Table 1

Ausgangs- zustand 	2 Mt/ 20°C	24 h/ 60°C	24 h/ 80°C	24 h/ 120°C
82	75,4	68,9	83,6	72,2
73,8	67,2	65,6	75,4	68,9
65,6	60,7	59,0	64,0	54,1
50,8	45,9	52,5	55,8	49,2
54,1	45,9	52,5	55,8	44,3
19,7	24,6	29,5	37,7	19,7
32,8	21,3	24,6	29,5	16,4
19,7	14,8	14,8	26,2	16,4
9,8	9,8	13,1	16,4	11,5
6,6	6,6	11,5	11,5	9,8
0	0	6,6	8,2	4,9

Key: a) Initial state

The first column contains the values for the freshly prepared sample, measured at room temperature, while column 2 shows the same measurement, repeated after 2 months of storage time. The remaining columns correspond to the measurement series following storage at the temperatures indicated in the first line. If the values from columns

2 through 5 are plotted against those in column 1, then a straight line of slope 1 is obtained. Thus, the gray scale values do not change under the influence of elevated temperatures.

1. The use of surface structures made of photo-addressable polymers having an optical anisotropy, Δn , of 0.001 to 0.95 for storing optically available information by partially selective variation of the optical anisotropy.

2. Use as recited in Claim 1 as holographic recording material.

3. A method for storing patterns in the surface structures to be used as recited in Claim 1 by exposure to light having an energy density of 103 to 107 mJ/m² for a period of 10⁻³ to 10⁻¹⁵ s.

4. Polymers in which pretreatment can produce optical anisotropy, which can be varied by exposure for a period of 10⁻³ to 10⁻¹⁵ s.

5. Polymers as recited in Claim 4, having side chains of various types on a main chain, which serves as a backbone, both of which can absorb electromagnetic radiation (at least for one type: preferably having the wavelength of visible light), provided that the absorption peaks of the different side chains are at a distance of at least 200 and no more than 10,000 cm⁻¹ from one another.

6. Polymers as recited in Claim 5, having side groups of the formulas:

-S¹-T¹-Q¹-A (I) and

-S²-T²-Q²-P (II),

where

S¹, S², independently of one another, mean oxygen, sulfur, or NR¹,

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R¹ is hydrogen or C₁-C₄ alkyl,

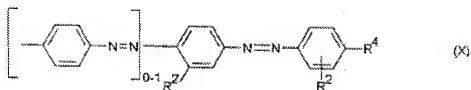
T¹, T², independently of one another, are the radical (CH₂)_n, which can optionally be interrupted by -O-, -NR¹-, or -OSiR¹₂O and/or optionally substituted with methyl or ethyl,

n is the number 2, 3, or 4,

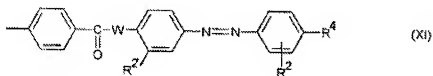
Q¹, Q², independently of one another, are a divalent radical,

A, P, independently of one another, are a unit capable of absorbing electromagnetic radiation.

7. Polymers as recited in Claims 4 through 6, wherein A and P correspond to the formulas:



and



where

R² is hydrogen or cyano,

R^{2'} is hydrogen or methyl,

W is oxygen or NR¹, and

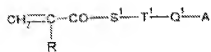
R⁴ is nitro, cyano, benzamido, p-chloro-, p-cyano-, p-nitrobenzamido, or dimethylamino.

8. Polymers as recited in Claims 4 through 7, wherein the groups -S¹-T¹-Q¹- and -S²-T²-Q²- correspond to the formulas -OCH₂CH₂O-, -OCH₂CH₂OCH₂CH₂O-, and -OCH₂CH₂-NR¹-.

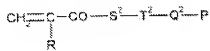
9. Polymers as recited in Claims 4 through 23, wherein the main chain is a poly(meth)acryloyl.

10. Polymers as recited Claims 4 through 9, into which double refraction changes, Δn, of over 0.15 can be inscribed with polarized light.

11. A method of producing polymers as recited in Claims 4 through 10, wherein monomers of the formulas



and



and

optionally additional monomers are copolymerized with one another.

12. Films of polymers as recited in Claims 4 through 10.

13. Substrates coated with films as recited in Claim 12.

14. The use of polymers as recited in Claims 4 through 10 for producing optical components.

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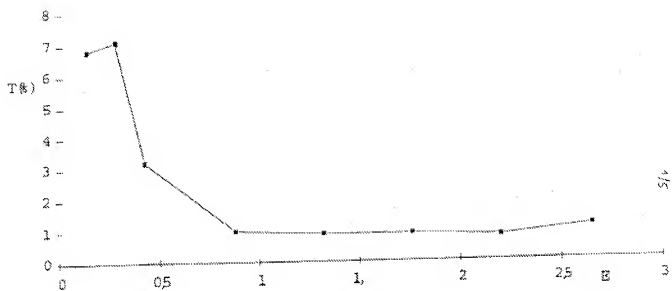


Fig. 1

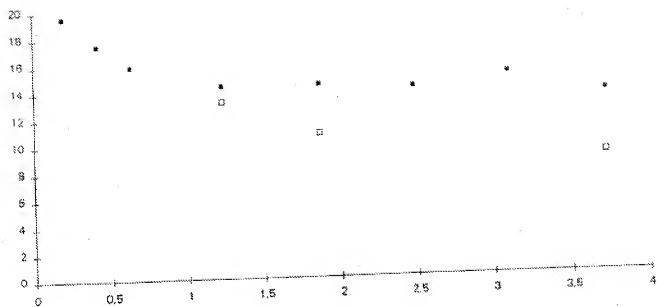


Fig 2

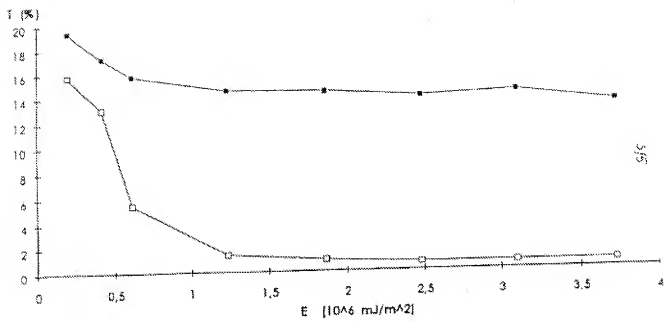


Fig. 3

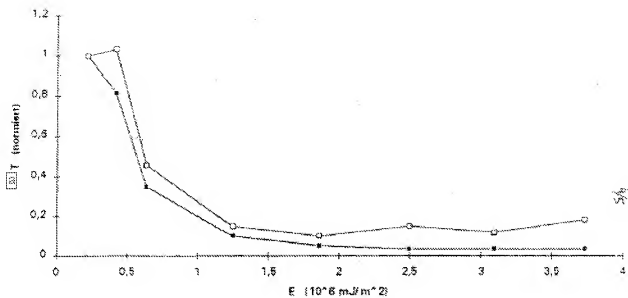


Fig 4

Key: a) T (normalized)

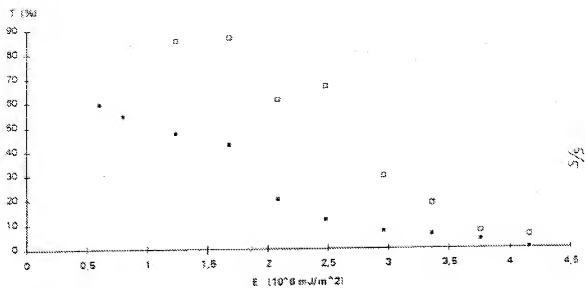


Fig. 5